

PRELIMINARY REPORT ON U-Th-Pb ISOTOPE SYSTEMATICS OF THE OLIVINE-PHYRIC SHERGOTTITE TISSINT. R. Moriwaki¹, T. Usui¹, T. Yokoyama¹, J. I. Simon², and J. H. Jones³, ¹Dept. of Earth and Planet. Sci., Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8551, Japan (moriwaki.r.ab@m.titech.ac.jp), ²Center for Isotope Cosmochemistry and Geochronology at ARES, NASA-JSC, Houston, TX 77058, USA, ³ARES, NASA-JSC, Houston, TX 77058, USA.

Introduction: Geochemical studies of shergottites suggest that their parental magmas reflect mixtures between at least two distinct geochemical source reservoirs, producing correlations between radiogenic isotope compositions, and trace element abundances [e.g., 1-3]. These correlations have been interpreted as indicating the presence of a reduced, incompatible-element-depleted reservoir and an oxidized, incompatible-element-rich reservoir. The former is clearly a depleted mantle source, but there has been a long debate regarding the origin of the enriched reservoir. Two contrasting models have been proposed regarding the location and mixing process of the two geochemical source reservoirs: (1) assimilation of oxidized crust by mantle derived, reduced magmas [2], or (2) mixing of two distinct mantle reservoirs during melting [3]. The former clearly requires the ancient martian crust to be the enriched source (crustal assimilation), whereas the latter requires a long-lived enriched mantle domain that probably originated from residual melts formed during solidification of a magma ocean (heterogeneous mantle model).

This study conducts Pb isotope and U-Th-Pb concentration analyses of the olivine-phyric shergottite Tissint because U-Th-Pb isotope systematics have been intensively used as a powerful radiogenic tracer to characterize old crust/sediment components in mantle-derived, terrestrial oceanic island basalts [4]. The U-Th-Pb analyses are applied to sequential acid leaching fractions obtained from Tissint whole-rock powder in order to search for Pb isotopic source components in Tissint magma. Here we report preliminary results of the U-Th-Pb analyses of acid leachates and a residue, and propose the possibility that Tissint would have experienced minor assimilation of old martian crust.

Sample: Tissint is the first witnessed fall of olivine-phyric shergottite [5], consisting of megacrysts of olivine and prismatically zoned pyroxene crystals. The whole-rock composition exhibits a geochemically depleted signature; e.g., $\epsilon^{143}\text{Nd} = +41.9$ at the time of crystallization ~ 596 Ma [6].

Analytical Method: We performed a 6-step sequential acid leaching experiment (Table 1) with 173 mg of Tissint whole-rock powder prepared in our clean lab at Tokyo Tech. Each fraction of acid leachate (L1-5) and residue (R) is split into one to nine. The 10% solution was used for trace element analysis by a

quadrupole type ICP-MS (X series II, Thermo-Fisher Scientific), while the 90% solution was held for Pb isotope analysis by a TIMS (Thermo-Fisher Scientific, Triton-*p/us*) at Tokyo Tech. The trace element analysis shows that only the L3, L5, and R fractions contain sufficient Pb for the precise isotopic measurements by TIMS. The analytical protocols for chemical purification and mass spectrometry using the ^{207}Pb - ^{204}Pb double spike method followed Kuritani and Nakamura [7,8]. The average for the NIST SRM981 standard measured over the last ~ 6 months in our laboratory yielded $^{206}\text{Pb}/^{204}\text{Pb} = 16.932$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.486$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.683$, respectively.

Table 1. Protocol of acid leaching experiment

Step	Reagent	Heating Time*	Temperature
L1	H ₂ O	30min	$\sim 20^\circ\text{C}$ (room temp).
L2	acetone	30min	$\sim 20^\circ\text{C}$ (room temp)
L3	0.5M HBr	1h	100°C
L4	1M HF	1h	120°C
L5	5M HCl	1h	120°C
R	Dissolved in HF and HBr for Pb isotope analysis (+HClO ₄ for trace element)		

*Each heating step follows a 30 min. ultrasonic experiment.

Results and Discussion: Trace element abundances in the acid leachate and residue are normalized to the Tissint whole-rock abundances [5], in order to examine what phases contributed to the trace element and U-Th-Pb isotopic compositions of these fractions. L3, L5 and the residue have higher REE (and other trace element) abundances than the other fractions (Fig. 1). L3 has a LREE-enriched pattern ($[\text{La}/\text{Lu}]_{\text{N}} = 2.0$) with a negative Eu anomaly ($\text{Eu}^* = 0.8$), whereas L5 and the residue exhibit prominent positive Eu anomalies ($\text{Eu}^* = 2.7$ and 1.6 , respectively). These REE signatures imply that L3 probably reflects residual melt after the crystallization of plagioclase (and olivine + pyroxene). In contrast, L5 and the residue are interpreted as representing early crystallization phases (plagioclase, pigeonite, olivine with melt inclusions).

Initial Pb isotopic compositions of leachate and residue are calculated based on the assumption that Tissint has a crystallization age of 596 Ma [6]. Some previous chronological studies based on the ^{207}Pb -

^{206}Pb isotopic systematics have proposed ancient crystallization ages for the shergottite suite (e.g., 4.3 Ga and 4.1 Ga for the geochemically depleted and enriched shergottites, respectively [e.g., 9]). We employ the young Sm–Nd internal isochron ages for Tissint and the other shergottites discussed in this study, because these Sm–Nd ages are consistent with Lu–Hf and Rb–Sr internal isochron ages [e.g., 6].

The leachate (L3 and L5) and residue have different initial Pb isotopic compositions: least radiogenic for the residue to moderate for L5 and the most radiogenic for L3 (Fig. 2). Interestingly, L3 plots on the compositional field of the enriched shergottites, while the residue plots on the depleted shergottite field. The geochemically enriched signature of L3 is also observed in the ^{238}U – ^{206}Pb isochron diagram (Fig. 2). Although the μ -value ($^{238}\text{U}/^{204}\text{Pb}$) is thought to be modified during the acid leaching experiment, such U–Pb fractionation does not significantly affect the fact that L3 and the enriched shergottites have the similar initial Pb isotopic compositions because the 596 Ma reference isochron has a very shallow slope within the compositional range of Fig. 2.

The radiogenic Pb isotopic signature of L3 could be explained by contamination of terrestrial Pb. Although our preliminary results cannot exclude this possibility, it is unlikely that L3 contains enough terrestrial Pb so that it completely overwrites the pristine, depleted isotopic composition by the measured, enriched composition. This is justified because: (1) Tissint is a “fall” meteorite (i.e., relatively less contaminated) and (2) mass balance calculation based on the ICP–MC data indicates that >10% of the total Pb in the original Tissint whole-rock powder was fractionated into the first two leaching steps (L1 and L2).

An alternative possibility is that Tissint had at least two geochemical components (enriched and depleted) at the time of eruption. If this inference is correct, our preliminary Pb isotope results suggest that Tissint acquired a geochemically enriched component during the latest stage of magmatic activity (i.e., crustal assimilation), because the enriched and radiogenic Pb component is observed in L3 that is interpreted as representing a residual melt, while the residue exhibits the geochemically depleted signature. The effect of crustal assimilation on Tissint magma might have been reflected by a slightly lower $\epsilon^{143}\text{Nd}$ value (+41.9) than the other depleted shergottites such as QUE 94210 ($\epsilon^{143}\text{Nd} = +47.6$) [10]. Our preliminary investigation demonstrates the potential of our methodology to constrain the two contrasting models regarding the location and mixing processes of the shergottite geochemical source reservoirs.

References: [1] Treiman, A.H. (2003) *Meteorit. Planet. Sci.*, 38, 1849–1864. [2] Wadhwa, M. (2001) *Science*, 291, 1527–1530. [3] Borg, L.E. and Draper, D.S. (2003) *Meteorit. Planet. Sci.*, 38, 1713–1731. [4] Hofmann, A. W. (2003) *Oxford, Elsevier-Pergamon*, 2: 61–101. [5] Chennaoui Aoudjehane, H. et al. (2012) *Science*, 338, 785–788. [6] Brennecka, G.A. et al. (2012) *75th MetSoc, Cairns*, Abs#5038. [7] Kuritani, T. and Nakamura, E. (2002) *Chemical Geology*, 186, 31–43 [8] Kuritani, T. and Nakamura, E. (2003) *JAAS*, 18, 1464–1470. [9] Bouvier, A. et al. (2009) *EPSL*, 280, 285–295. [10] Borg, L.E. et al. (1997) *GCA*, 61, 4915–4931.

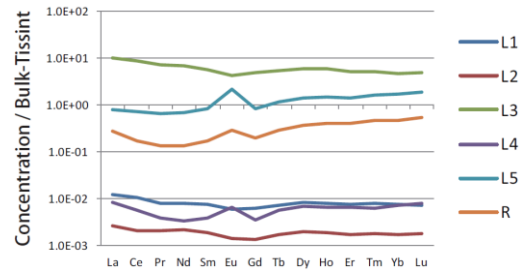


Fig 1. REE patterns of the acid leaching fractions.

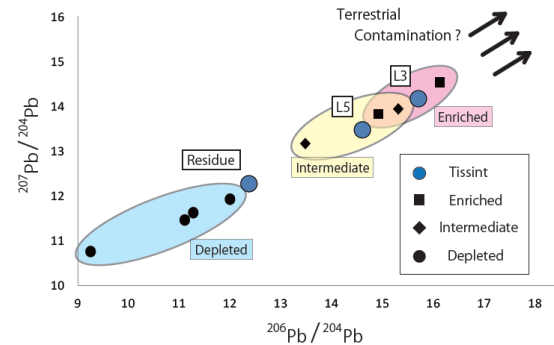


Fig 2. Initial Pb isotopic compositions of the Tissint leachate and residue. Whole-rock Pb isotopic compositions of other shergottites are also shown.

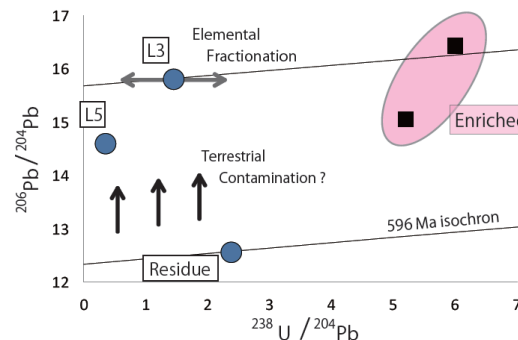


Fig 3. ^{238}U – ^{206}Pb isochron diagram for Tissint leachate and residue. Black arrows indicate an expected trajectory for the effect of terrestrial Pb contamination. Elemental fractionation during acid leaching does not change Pb isotopic composition (gray arrow).